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Natural gas — Supporting information on the calculation of physical properties according to ISO 6976

Gaz naturel — Informations supplémentaires pour le calcul des propriétés physiques selon l'ISO 6976

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

Introduction

Both international and intranational custody transfer of natural gas usually require precise determination of both the quantity and the quality of the gas to be traded. ISO 6976:2016, which cancels and replaces ISO 6976:1995, specifies methods for the calculation of those properties, often known as the combustion properties, which (in part) describe gas quality, namely gross (superior) and net (inferior) calorific value, density, relative density, gross and net Wobbe index. The methods provide the means of calculating the properties, including uncertainties, of any natural gas, natural gas substitute, or similar combustible gaseous fuel of known composition at commonly used reference conditions.

Some 80-odd years ago, in the Introduction to Hyde and Mills' classic text *Gas Calorimetry*, Sir Charles Vernon ('CV') Boys wrote the words[109] " ... *I hesitate to give the number of actual tests of the calorific value of gas which are made every year, but ... it will be evident that any machinery set up to ascertain its value must be extensive ... The fact is that no single commodity generally purchased by the public is so carefully watched and maintained of its guaranteed quality as gas ...* ". Since that time, the technology of gas calorimetry has changed beyond either recognition or imagination, but the truth of the sentiment expressed remains unchanged and refers every bit as much to 2017 as it did to 1932.

This document acts as a repository for those manifold technical details which justify and explain the methods presented in the new third (2016) edition of ISO 6976 but which are not directly needed in its everyday routine implementation. In short, it is conceived and intended as a complete(ish) knowledge base which provides full and proper technical authentication of ISO 6976.

Natural gas — Supporting information on the calculation of physical properties according to ISO 6976

1 Scope

This document acts as a repository for those manifold technical details which justify and explain the methods presented in the third edition of ISO 6976 but which are not directly needed in the everyday routine implementation of the standard.

Each main clause addresses a specific aspect of the calculational method described in ISO 6976:2016, and is intended to be self-sufficient and essentially independent of each other clause. For this reason, the user should not expect the whole to be accessible to study as a sequentially coherent narrative.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6976 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

4 Symbols, units and abbreviated terms

4.1 Quantities

Symbol	Meaning	Unit
a	atomic index for carbon in the generalized molecular species $C_aH_bN_cO_dS_e$	—
b	atomic index for hydrogen in the generalized molecular species $C_aH_bN_cO_dS_e$	—
c	atomic index for nitrogen in the generalized molecular species $C_aH_bN_cO_dS_e$	—
d	atomic index for oxygen in the generalized molecular species $C_aH_bN_cO_dS_e$	—
e	atomic index for sulfur in the generalized molecular species $C_aH_bN_cO_dS_e$	—
g	coefficients in equation for B	—
h	molar enthalpy	$kJ \cdot mol^{-1}$
k	coverage factor	—
m	number of sets of values	—
n	number of determinations in a set of values	—
p	pressure (absolute)	kPa
q	exact input quantity in calculation of Y	(varies)
r	correlation coefficient	—
s	summation factor	—
t	Celsius temperature	°C
$u(Y)$	standard uncertainty of Y	(varies)

Symbol	Meaning	Unit
$u(Y,Y')$	covariance of Y and Y'	(varies)
w	repeatability or reproducibility	(varies)
x	mole fraction	—
y	inexact input quantity in calculation of Y	(varies)
A	atomic mass (atomic weight)	kg·kmol^{-1}
B	second virial coefficient	m^{3}·mol^{-1}
C	third virial coefficient	m^{6}·mol^{-2}
Cp	molar isobaric heat capacity	kJ·mol^{-1}·K^{-1}
D	(mass) density	kg·m^{-3}
$Đ$	molar density	mol·m^{-3}
E	non-random (systematic) bias from the true value of Hc	kJ·mol^{-1}
F	function that generates property Y	—
G	relative density	—
Hc	molar-basis calorific value (negative enthalpy of combustion)	kJ·mol^{-1}
Hf	enthalpy of formation	kJ·mol^{-1}
Hm	mass-basis calorific value	MJ·kg^{-1}
Hv	volume-basis calorific value	MJ·m^{-3}
J	j-th virial coefficient	m$^{3(j-1)}$·mol$^{-(j-1)}$
L	molar enthalpy of vaporization of water	kJ·mol^{-1}
M	molar mass (molecular weight)	kg·kmol^{-1}
N	number of components in a mixture	—
	number of input values of y	—
Q	amount of heat released	kJ·mol^{-1}
R	molar gas constant	J·mol^{-1}·K^{-1}
S	sum of mole fractions (= 1)	—
T	thermodynamic (absolute) temperature	K
$U(Y)$	expanded uncertainty of Y	(varies)
V	molar volume	m^{3}·mol^{-1}
W	Wobbe index	MJ·m^{-3}
Y	general (unspecified) physical property	(varies)
Z	compression factor	—
α	mole fraction of nitrogen in dry combustion air	—
β	mole fraction of oxygen in dry combustion air	—
γ	mole fraction of argon in dry combustion air	—
δ	mole fraction of water vapour in humid combustion air	—
ε	molar amount of air (including any excess) per mole of reactant	—
ζ	zero-value parameter having non-zero uncertainty	—
η	unity-value factor having non-zero uncertainty	—
θ	$a + b/4$	—
λ	random contribution of offset from the true value of Hc	kJ·mol^{-1}
μ	dipole moment	debyes
ν	stoichiometric coefficient	—
ξ	relative humidity	—
τ	100 K/T	—
φ	molar amount of saturated exhaust gases per mole of reactant	—

Symbol	Meaning	Unit
ω	acentric factor	—
$\Lambda_{1\text{-}9}$	constants in the Aly-Lee Cp^{o} formulation	—
Φ	function that generates the third term of a virial expansion	—

4.2 Subscripts

c	at the gas-liquid critical point
g	for the sample gas
i	serial counter
	component identifier
j	serial counter
	component identifier
k	serial counter
m	serial counter
n	serial counter
r	value made dimensionless (reduced) using values for the gas-liquid critical properties
s	at the vapour-liquid saturation point
w	for water vapour
G	gross/superior (calorific value or Wobbe index)
N	net/inferior (calorific value or Wobbe index)
air	for air
0	reference (base) value of pressure or temperature
1	combustion reference state/condition
2	metering reference state/condition

4.3 Superscripts

o	for the ideal gas state
*	pre-normalization value
+	modified value

4.4 Abbreviated terms

liq	liquid
ppm	parts per million (moles per million moles)
sat	saturated with water vapour
vap	vapour
AGA	American Gas Association (USA)
BAM	Bundesanstalt für Materialforschung und Prüfung (Germany)
BBC	British Broadcasting Corporation (UK)
CIAAW	IUPAC Commission on Isotopic Abundances and Atomic Weights
GERG	Groupe Européen de Recherches Gazières
GOMB	Gas and Oil Measurement Branch (UK Department of Energy)
GPA	Gas Processors Association (USA)
IAPWS	International Association for the Properties of Water and Steam
IGT	Institute of Gas Technology (USA)
IUPAC	International Union of Pure and Applied Chemistry

NAMAS	National Measurement Accreditation Service (UK)
NBS	National Bureau of Standards (U.S. Department of Commerce)
NIST	National Institute of Standards and Technology (U.S. Department of Commerce)
NPL	National Physical Laboratory (UK)
OFGEM	Office of Gas and Electricity Markets (UK National Regulatory Authority)
PTB	Physikalische-Technische Bundesanstalt (Germany)
PVT	pressure-volume-temperature
SD	standard deviation
SE	experimental standard deviation of the mean (standard error)
SI	Système Internationale des Unités
UKAS	United Kingdom Accreditation Service (UK)

5 Enthalpy of combustion of the ideal gas and its variation with temperature

5.1 Preamble

The most fundamental thermophysical properties required in the calculation of the calorific values of a gas or gas mixture are the ideal-gas (standard) enthalpies of combustion $(-Hc^o)_j$ of each of its component molecular species at any temperature at which combustion may be deemed to take place, i.e. the combustion reference temperature.

In ISO 6976:2016, 6.1, the user is advised that each of these quantities $(-Hc^o)_j$, equal numerically to the corresponding ideal-gas gross (superior) calorific value $(Hc)_G^o$ of component *j* varies, albeit weakly, with the combustion reference temperature. The variation observed is nevertheless significant and cannot be ignored in the kind of high-precision calculations that are made possible by ISO 6976.

The theoretical variation of Hc^o with temperature is in general mathematically unwieldy and, in consequence, it is not practicable to provide simple formulations that would enable the user to determine Hc^o at any arbitrary combustion reference temperature. Instead, values of $(Hc^o)_j$ for each distinct molecular species *j* listed in ISO 6976 are given in ISO 6976, Table 3 for each of the commonly used combustion reference temperatures of 298,15 K, 293,15 K, 288,71 K, 288,15 K and 273,15 K (25 °C, 20 °C, 60 °F, 15 °C and 0 °C, respectively).

The first of these temperatures, 298,15 K, is the temperature adopted by the International Union of Pure and Applied Chemistry (IUPAC) as the reference temperature for thermochemistry and, in consequence, critically evaluated values of $Hc^o(25)$ are readily available in the published scientific literature.

Values of Hc^o have therefore been carefully selected for each of the chemical species listed in ISO 6976:2016 at this temperature (see 5.2), and used as the basis for the calculation of values for the other temperatures as described below (see 5.3 and 5.4).

5.2 Standard enthalpy of combustion at 25 °C

Except for methane, for which a new and specially detailed re-evaluation is given in Clause 11 and for water (changed by a trivially small amount in accordance with the latest IAPWS documentation[3]), the values of $Hc^o(25)$ listed in ISO 6976:2016, Table 3 are unchanged from those given in ISO 6976:1995. All of these values were, in turn, taken from fully-referenced tabulations in GERG TPC/1[4], the major sources for which were Garvin et al.[5] and tables published by the Thermodynamics Research Center[6].

For those components new to the third edition of ISO 6976, namely n-undecane, n-dodecane, n-tridecane, n-tetradecane and n-pentadecane, values of $Hc^o(25)$ have been taken without change from[6].

5.3 Standard enthalpy of combustion at other temperatures

The values listed in ISO 6976:2016, Table 3 for temperatures other than 25 °C have been derived as follows.

Consider the generalized combustion reaction for the pure, supposedly gaseous, chemical species $C_aH_bN_cO_dS_e$, in which the atomic indices *a* to *e* are small non-negative integers (including zero) whose values define the specific species in question (e.g. for *a* = 1, *b* = 4, *c* = *d* = *e* = 0, the species is CH_4), *viz.*

$$C_aH_bN_cO_dS_e(g) + (a + b/4 - d/2 + e)\ O_2(g) = a\ CO_2(g) + b/2\ H_2O(liq) + c/2\ N_2(g) + e\ SO_2(g) \tag{1}$$

NOTE In some applications, it might be better to consider any sulfur in the products of combustion to be present as H_2SO_4, either gaseous or liquid as appropriate but, in the present application, gaseous sulfur dioxide is the likely product.

Suppose that the standard enthalpy of combustion at 25 °C, $-Hc^o(25)$, for this reaction is available in authoritative publications (as is indeed the case for all species considered herein). The value of $Hc^o(t)$ at some other temperature *t*, for this same species *j*, is then given by

$$[-Hc^o(t)]_j = [-Hc^o(t_0)]_j + \sum_i \nu_i \times [h_i^o(t_0) - h_i^o(t)] \tag{2}$$

or, equivalently,

$$[-Hc^o(t)]_j = [-Hc^o(t_0)]_j + \sum_i \int_t^{t_0} \nu_i \times (Cp^o)_i \,\mathrm{d}t \tag{3}$$

where

t_0 is equal to 25 °C;

$h_i^o(t)$ is the ideal-gas molar enthalpy of component *i*;

$(Cp^o)_i$ is the ideal-gas isobaric molar heat capacity of component *i* (except for product water which is taken as the liquid);

ν_i is the stoichiometric coefficient for component *i*, being taken as positive for reactants (unity for the "object" species *j*) and negative for products.

The summation is taken over all species *i* (including *j*) that appear in the combustion reaction (a maximum of 6 in the most general case).

For convenience, we may set

a) *i* = 1 for the combusted species *j*, from which it follows that ν_1 = 1 for all *j*,

b) *i* = 2 for the reactant oxygen, whence $\nu_2 = [a+(b/4)-(d/2)+e]$,

c) *i* = 3 for the product carbon dioxide, whence $\nu_3 = -a$,

d) *i* = 4 for the product water, whence $\nu_4 = -b/2$,

e) *i* = 5 for any product nitrogen, whence $\nu_5 = -c/2$, and

f) *i* = 6 for any product sulfur dioxide, whence $\nu_6 = -e$.

Thus, the calculation is reduced to having sufficient knowledge of either h^o or, equivalently, Cp^o as a function of temperature, for the "object" species *j* and for the 5 "auxiliary" species O_2, CO_2, N_2 and SO_2 (in the gas phase) and liquid water. Either quantity is a complicated function of temperature, historically often expressed in polynomial form, for all molecular species.

5.4 Formulation of the ideal-gas enthalpy

Appropriate data for the enthalpy differences $[h_i^o(t_0) - h_i^o(t)]$ between specific temperatures, which thus enable direct calculations of $Hc^o(t)$, without recourse to polynomial expressions, may be found for several of the present components in the compilations of Armstrong and Jobe[7] and (less explicitly) of Garvin et al.[5][8] For components not considered in these sources recourse is indeed necessary to polynomial expressions that are available in the research literature.

Several types of polynomial expression have been used over the years to represent the variation of h^o and Cp^o with temperature. For the present application, the temperature range over which the variation is needed is rather small (a maximum of 25 K). Partially as a consequence of this, the entire second term on the right-hand side of Formulae (2) and (3) is very small by comparison with the leading term, and any reasonable formulation should produce essentially identical results for $Hc^o(t)$. Polynomials of the simple functional form given by Passut and Danner[9] (a power series in absolute temperature *T*) or of the somewhat more complex modified Wilhoit-Harmens form[10][11][12] are available for a very wide range of molecular species.

For preliminary investigations in ISO 6976:1995, calculations for $Hc^o(t)$ were, wherever possible, carried out by a variety of routes in order to confirm their equivalence. No significant discrepancies were revealed - that is, differences were generally only to be found at the level of hundredths of kJ·mol^{-1} (the second place of decimal in ISO 6976:2016, Table 3). This level of uncertainty is usually not significant in terms of either measurement accuracy or the required precision of calculation, and the second place of decimal is retained in Table 3 only for interpolative purposes.

Since somewhat before (but not used in) the preparation of the second edition of ISO 6976, a more complex formulation for $h^o(T)$ and $Cp^o(T)$ has become available through the publications of Lee et al. [13][14][15], reproduced here for Cp^o as Formula (4).

$$\frac{Cp^o(T)}{R} = \Lambda_1 + \Lambda_2 \cdot \left(\frac{\Lambda_3 / T}{\sinh(\Lambda_3 / T)}\right)^2 + \Lambda_4 \cdot \left(\frac{\Lambda_5 / T}{\cosh(\Lambda_5 / T)}\right)^2 + \Lambda_6 \cdot \left(\frac{\Lambda_7 / T}{\sinh(\Lambda_7 / T)}\right)^2 + \Lambda_8 \cdot \left(\frac{\Lambda_9 / T}{\cosh(\Lambda_9 / T)}\right)^2 \quad (4)$$

This formulation, involving the use of hyperbolic functions, has gained much popularity and has been applied to many components of natural gas by Jaeschke and Schley[16], who give values of the constants $\Lambda_{1\text{-}9}$ for each of these components. Furthermore, it has been incorporated into the methodology given in ISO 20765-1:2005[17] and ISO 20765-2:2015[18] for the calculation of thermodynamic properties of natural gas.

For this reason, the Aly-Lee method, as implemented in the commercially available thermophysical properties computer package GasVLe®[1)], has been used for the purpose of deriving final values of $Hc^o(20)$, $Hc^o(15{,}55)$, $Hc^o(15)$ and $Hc^o(0)$ from $Hc^o(25)$ to list in ISO 6976:2016, Table 3. In general, the values so derived are unchanged from those listed in ISO 6976:1995, Table 3, but in a few cases there are trivial changes of one or two hundredths of kJ·mol^{-1}.

1) GasVLe® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

5.5 Illustrative examples

Figure 1 is an example, in this case for methane, of how conversion from standard enthalpy of combustion at 25 °C (assumed known) to the corresponding value at 15 °C is carried out. The calculation is performed in accordance with Formula (2) and is presented in Figure 1 in a simple flowsheet-cum-spreadsheet style layout. All the values of $[h^o(25) - h^o(15)]$ are taken directly from tabulations given in Armstrong and Jobe[7]. No further explanation seems to be necessary.

Another example is given as Figure 2, in this case for hydrogen sulfide, a non-hydrocarbon for which not all of the required data are available in Armstrong and Jobe. This time the conversion is carried out from 25 °C to 0 °C. In this example, of course, the products include sulfur dioxide but no carbon dioxide, and not all of the stoichiometric coefficients are integral. This time the values of $[h^o(25) - h^o(0)]$ have mostly been calculated using the modified Wilhoit-Harmens formulation[12], as formerly implemented in the computer package GasVLe®.

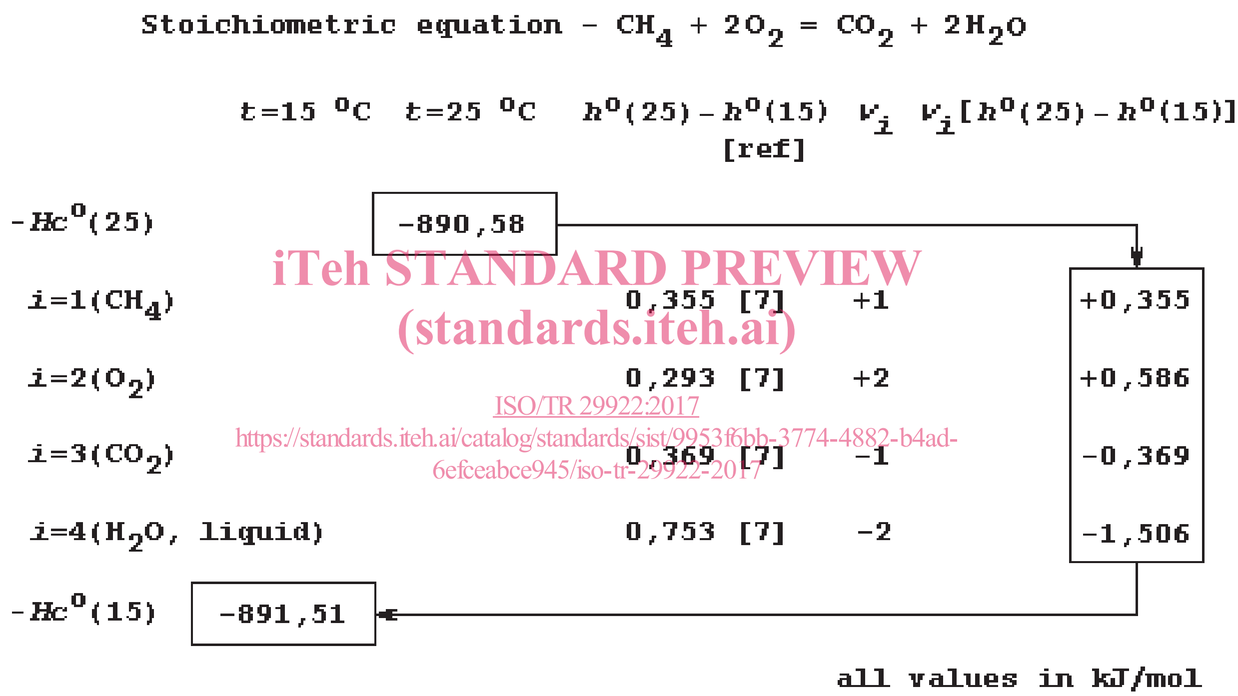

Figure 1 — Conversion of the enthalpy of combustion of the ideal gas from 25 °C to 15 °C — Methane

